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SYNTHESIS AND NMR STUDY OF ETHYL- AND PERFLUORO-ETHYL TIN VINYL --ETC(U)

AUG 78 S E ULRICH, J J ZUCKERMAN

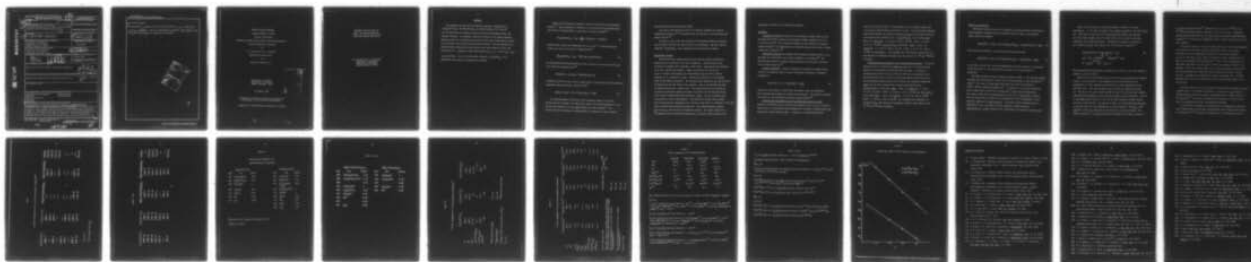
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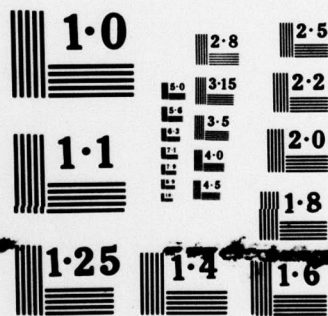
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1. REPORT NUMBER 5	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Synthesis and NMR Study of Ethyl- and Perfluoroethyltin Vinyl and Hydride Derivatives.		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) S. E. Ulrich and J. J. Zuckerman		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Oklahoma Department of Chemistry Norman, Oklahoma 73019		7. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0432
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-636
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12/25p. LEVEL II		12. REPORT DATE 16 August, 1978
		13. NUMBER OF PAGES 22
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Prepared for Publication in Inorganica Chimica Acta		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Tetrasubstituted Organotins Fluorine-19 Nmr Ethyltins Ethylstannanes Perfluoroethyltins Vinyltins Proton Nmr		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The syntheses of four perfluoroethyltin compounds, $(C_2H_5)_2Sn(C_2F_5)_2$, $(C_2H_5)_2Sn(I)C_2F_5$, $(CH_2=CH)_2Sn(C_2F_5)_2$ and $(CH_2=CH)_3SnC_2F_5$, are reported for the first time via a Barbier reaction from the corresponding ethyl- and vinyltin bromides. The synthetic reactions resulted in the iodide transhalogenation product in the ethyltin case and the vinyl group redistribution product in the vinyltin case as well as the expected products. The new compounds were characterized by infrared and mass spectral data, and studied by proton and		

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Task No. NR 053-636

Synthesis and NMR Study of Ethyl- and Perfluoroethyltin

Vinyl and Hydride Derivatives

by

S. E. Ulrich and J. J. Zuckerman

Prepared for Publication

in

Inorganica Chimica Acta

University of Oklahoma
Department of Chemistry
Norman, Oklahoma 73019

16 August, 1978

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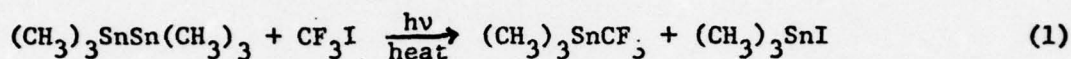
SYNTHESIS AND NMR STUDY OF
ETHYL- AND PERFLUOROETHYL TIN
VINYL AND HYDRIDE DERIVATIVES

S.E. Ulrich¹ and J.J. Zuckerman^{*}
Department of Chemistry
University of Oklahoma
Norman, Oklahoma 73019

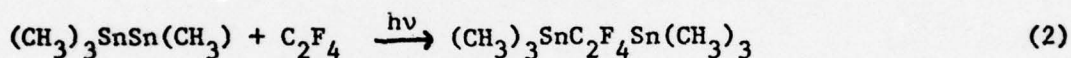
ABSTRACT

The syntheses of four perfluoroethyltin compounds, $(C_2H_5)_2Sn(C_2F_5)_2$, $(C_2H_5)_2Sn(I)C_2F_5$, $(CH_2=CH)_2Sn(C_2F_5)_2$ and $(CH_2=CH)_3SnC_2F_5$, are reported for the first time via a Barbier reaction from the corresponding ethyl- and vinyltin bromides. The synthetic reactions resulted in the iodide transhalogenation product in the ethyltin case and the vinyl group redistribution product in the vinyltin case as well as the expected products. The new compounds were characterized by infrared and mass spectral data, and studied by proton and fluorine-19 nmr. Analyses of these data yielded the ν_A , ν_B , ν_E and $|J_{AB}|$, $|J_{AC}|$, $|J_{BC}|$ parameters. The four ethylstannane compounds, $(C_2H_5)_nSnH_{4-n}$, were synthesized and utilized in comparison nmr studies.

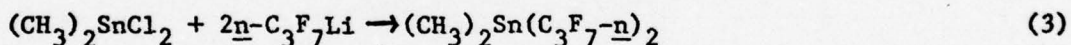
Among the tetraorganotin compounds, several are known with perfluoroalkyl groups.²⁻⁴ Their synthesis by cleavage of the tin-tin bond in hexamethylditin was discovered independently by two groups of workers in 1960:⁵⁻⁸



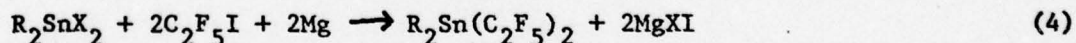
Perfluoroethyl iodide and hexaphenylditin also react.⁵ Tetrafluoroethylene inserts into the tin-tin bond of hexamethylditin:⁹



and dimethylbis(perfluoropropyl)tin has been prepared by treating the dichloride with perfluoro-n-propyllithium:¹⁰



A Barbier reaction has been used to prepare methyl- and n-butyltin perfluoroethyltin compounds using perfluoroethyl iodide in THF:¹¹



The perfluoroalkyltin derivatives lend themselves readily to study by fluorine-19 nmr techniques, and first-order spectra with large separations in the CF_2 and CF_3 resonances in these $\text{A}_3\text{B}_2\text{X}$ systems have been observed.¹² The fluorine-fluorine couplings in perfluoroethyltin compounds are small compared

with those found in perfluoroethyl iodide.

The study of the proton nmr spectra of vinyltin compounds has received considerable attention,¹³⁻¹⁸ including those tin derivatives with perfluoroalkyl groups attached.¹⁹

We report in this paper the synthesis of four perfluoroethyltin compounds not previously reported, and their study by nmr techniques. The four ethyltin compounds, $(C_2H_5)_nSnH_{4-n}$, were synthesized for comparison nmr studies.

Experimental Section

All materials were reagent grade and used without further purification. Operations were carried out in an inert atmosphere. Infrared spectra were recorded on a Beckman IR-10 using NaCl liquid cells. Mass spectra were obtained on an A.E.I. MS-902 spectrometer. Sample purification was carried out on an F + M Model 5750 Research Gas Chromatograph using an SE-30 packed $\frac{1}{2}$ " diameter, 30 ft, preparative column. Routine nmr spectra were run on Varian A-60A and HA-100D spectrometers. The stannanes were examined as ca. 20% solutions in benzene with TMS (ca. 20%) as the reference. Runs on the HA-100D were made in frequency sweep with a benzene lock. The chemical shifts were measured by counting the difference between the manual oscillator and the sweep oscillator with a Hewlett-Packard Model 521C electronic counter. The nmr parameters were calculated on a Univac 1108 computer. The fluorine-19 spectra were recorded with the spectrometer operating in the frequency sweep mode at a frequency of 94.1 MHz with a fluorotrichloromethane lock material. The perfluoroethyltin samples were run as ca. 20% solutions in methylene chloride. The larger range of the ¹⁹F chemical shifts necessitated substituting an external audio oscillator for

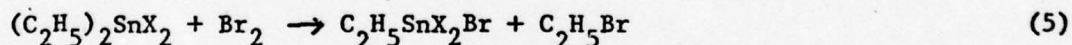
the manual oscillator of the HA-100D spectrometer.

Syntheses

Triethyltin hydride was prepared from triethyltin bromide which in turn was made from tin(IV) bromide and tetraethyltin (Alpha Inorganics, Inc.) in a 1:3 molar ratio.²⁰ The triethyltin bromide was then reduced with lithium aluminum hydride²¹ and identified by its infrared spectrum which shows a strong $\nu(\text{SnH})$ mode at 1820 cm^{-1} .²²

Diethyltin dihydride was prepared from diethyltin dibromide which in turn was made from tetraethyltin and tin(IV) bromide in a 1:1 mixture.²⁰ The dibromide was reduced by lithium aluminum hydride and the product identified by its infrared spectrum.²²

Ethyltin trihydride. Ethyltin trihalide was prepared by adding bromine slowly to an equimolar amount of molten diethyltin dichloride or dibromide according to:



The mixture was allowed to reflux until the bromine color was dissipated. The resulting ethyl bromide was removed by distillation. The ethyltin trihalide was reduced to the trihydride by lithium aluminum hydride.²³

Diethylbis(perfluoroethyl)tin and Diethylperfluoroethyltin Iodide.

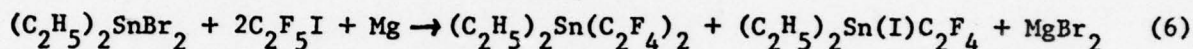
Diethyltin dibromide (15.9 g, 0.05 mol) and magnesium metal (2.4 g, 0.10 gm-at) were placed in a three-necked flask equipped with condensor, dropping funnel and stirrer and THF (200 ml) added. A solution of perfluoroethyl iodide

(24.6 g, 0.10 mol) in THF (50 ml) precooled to 0°C was added dropwise over 2 hrs and the reaction mixture stirred for 24 hrs. The precipitated magnesium salts were filtered, the volatiles stripped in vacuo and three major products were isolated and purified by glc.: $(C_2H_5)_2Sn(C_2F_5)_2$ in 10% yield, Anal.: Calcd. for $C_8H_{10}F_{10}Sn$: C, 23.15; H, 2.43; F, 45.80%. Found: C, 23.37; H, 2.37; F, 48.32%; $(C_2H_5)_2Sn(I)C_2F_5$ in 8% yield. Anal.: Calcd. for $C_6H_{10}F_5ISn$: C, 17.05; H, 2.38; F, 22.47%. Found: C, 17.27; H, 2.38; F, 22.41%; and $(C_2H_5)_2SnBr_2$. The compounds were identified by infrared (as ca. 10% solutions in methylene chloride), mass spectral and 1H , ^{19}F and ^{119}Sn nmr techniques.

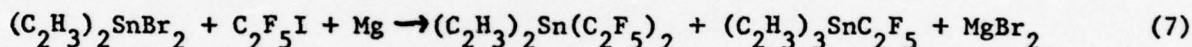
Divinylbis(perfluoroethyl)tin and Trivinylperfluoroethyltin. Divinyltin dibromide (16.6 g, 0.05 mol) and magnesium metal (2.4 g, 0.10 gm-at) were placed in a three-necked flask and THF (200 ml) added. A solution of perfluoroethyl iodide (24.6 g, 0.10 mol) in THF (50 ml) precooled to 0°C was added dropwise over 2 hrs and the reaction mixture stirred for 24 hrs. The precipitated magnesium salts were filtered, the volatiles stripped in vacuo, and two major products were isolated and purified by glc.: $(C_2H_3)_2Sn(C_2F_5)_2$ in 10% yield, Anal.: Calcd. for $C_8H_6F_{10}Sn$: C, 23.39; H, 1.47; F, 46.25%. Found: C, 23.44; H, 1.16; F, 45.96%; and $(C_2H_3)_3SnC_2F_5$ in 5% yield, Anal.: Calcd. for $C_8H_9F_5Sn$: C, 30.14, H, 2.84; F, 29.80%. Found: C, 30.73; H, 2.81; F, 28.37%. The compounds were identified by infrared (as ca. 10% solutions in methylene chloride), mass spectral, and 1H , ^{19}F and ^{119}Sn nmr techniques.

Results and Discussion

The Barbier reaction was used to synthesize the perfluoroethyltin derivatives. Using diethyltin dibromide with perfluoroethyl iodide in THF, a new organotin iodide derivative resulted:



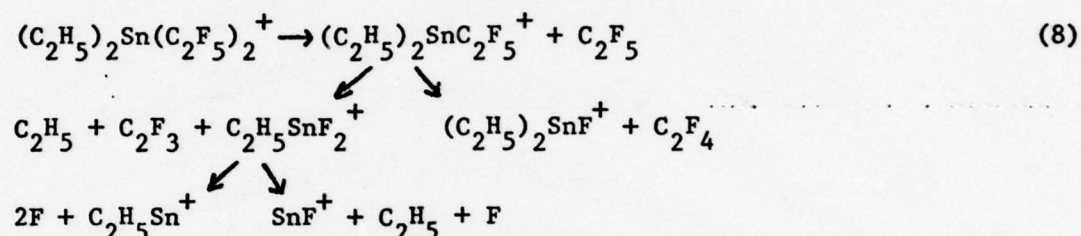
With divinyltin dibromide a new trivinyltin derivative resulted:



In the first reaction (Eq. 6) the transhalogenation reaction product is unexpected; in the second (Eq. 7) the redistribution reaction of the vinyl groups is unexpected.

The infrared data for these products are given in Table I. The perfluoroethyltin compounds show characteristic, strong $\nu(\text{C-F})$ stretching modes in the $1325\text{--}1050\text{ cm}^{-1}$ region.⁵ Four sets of strong bands associated with $\nu(\text{C-F})$ are observed at 1318 ± 5 , 1195 ± 10 , 1095 ± 10 and $1060\pm 10\text{ cm}^{-1}$. In addition, all the C_2F_5 derivatives have a single band at $927\pm 10\text{ cm}^{-1}$ arising from a carbon-carbon skeletal mode. The vinylic carbon-carbon stretching mode at 1915 cm^{-1} in $(\text{C}_2\text{H}_3)_3\text{SnC}_2\text{F}_5$ compares with the similar band at 1908 cm^{-1} in tetravinyltin,²⁴ but no absorption in this region was observed in $(\text{C}_2\text{H}_3)_2\text{Sn}(\text{C}_2\text{F}_5)_2$. The normal $\nu(\text{C-H})$ stretching modes at $3000\text{--}2800\text{ cm}^{-1}$ were also seen in all the compounds studied except for $(\text{C}_2\text{H}_3)_2\text{Sn}(\text{C}_2\text{F}_5)_2$, perhaps because of low concentration of the dilute solution used.

Table II lists the major tin-bearing fragments observed in the mass spectrometer. In all cases the highest mass fragment observed is the parent- C_2F_5^+ ion. That this is true as well for $(\text{C}_2\text{H}_5)_2\text{Sn}(\text{I})\text{C}_2\text{F}_5$ implies that C_2F_5 may be a more stable fragment than the iodine atom in the low density gas phase conditions in the mass spectrometer. Decomposition schemes are outlined in Eq. 8 below by analogy with proposals for other ethyltin compounds:²⁵



The same generalized decomposition pathways seem to hold for the vinyl compounds studied, as seen in Table 2.

Table III lists the fluorine-19 nmr data for the perfluoroethyltin compounds studied. The nmr spectra of tin compounds can be best described as the superposition of three subspectra arising from the three magnetically active isotopes of tin. Zero spin isotopes account for 85% of naturally occurring tin. The spin of one half tin-119 (8.68%) and tin-117 (7.67%) each add a doublet splitting with gyromagnetic ratios different enough to allow resolution. Tin-115 is also magnetically active ($I = \frac{1}{2}$), but its small abundance (0.35%) prevents its effect being observed. The spectra of ethyl- or perfluoroethyltin compounds is thus the result of the superposition of three subspectra: 85% A_3B_2 , 8.68% $\text{A}_3\text{B}_2\text{X}$ and 7.67% $\text{A}_3\text{B}_2\text{Y}$, which are in the proton nmr rarely first-order. The spectral analyses of the A_3B_2 portions were performed by the exact solution of

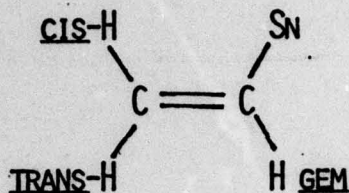
the secular equation method.²⁶ Observation of one set of $^{117,119}\text{Sn-A}$ and $^{117,119}\text{Sn-B}$ satellites permits evaluation of the two J values. Transition frequencies and intensities for the A_3B_2 system are obtained from experimental parameters.²⁷ The proton nmr assignments listed in Table IV were derived from this treatment.

The vinyltin system is of the three-spin ABC type so far as the nonmagnetic tin isotopes are concerned, and large second-order effects are present. Solutions for the six independent parameters in the secular equations, ν_A , ν_B , ν_C , and $|J_{AB}|$, $|J_{AC}|$, $|J_{BC}|$, were obtained using a modification²⁸ of Part I of the LAOCOON II Fortran Program.²⁹ Most of the tin satellites are observable, and these allow the chemical shifts and coupling constants to be estimated. Since the relative signs of the coupling constants can also alter the calculated spectrum, trials with various signs for the three J values were run. Convergence was achieved for the ABC centerbands only. The ABCX and ABCY systems are first-order because of the large chemical shifts of the tin isotopes.

The proton nmr spectra of the diethyltin perfluoroethyl derivatives closely resemble those of the diethyltin dihalides. An increase in δ_{AB} on going to $(C_2H_5)_2\text{Sn(I)C}_2F_5$ reflects the smaller electronegativity of iodine relative to the C_2F_5 group.³⁰ The values of $|J(\text{Sn-A})|$ and $|J(\text{Sn-B})|$ also fall into the range of couplings observed for the diethyltin dihalides.

In the vinyltin compounds it is observed that the trans-proton resonance moves progressively downfield when perfluoroethyl groups replace vinyl groups in tetravinyltin,¹⁴⁻¹⁶ and this is accompanied by a downfield shift of the

cis-proton resonance while the gem-proton resonance remains almost unchanged.



In $(C_2H_3)_2Sn(C_2F_5)_2$, $\nu_{trans} < \nu_{gem}$, but the order $\nu_{trans} > \nu_{cis} > \nu_{gem}$ has been observed in several hundred vinyl compounds.³¹ Anomalous orders have also been found for acrylonitrile³²⁻³³ and vinyl ethers.³⁴⁻³⁶ In vinyl ethers the high shifts are thought to arise from delocalization effects, while strong diamagnetic anisotropies associated with the triple bond are thought to cause the anomalous order of shifts in the nitrile. It has been suggested that anisotropies arising from the Sn-C bond act to deshield the vinyl protons in tetravinyltin in the order gem->trans->cis-.¹⁵ Since the order in the vinyltin compounds studied here is trans $\nu_{trans} \approx \nu_{cis} > \nu_{gem}$, the bond anisotropies do not predominate.

The effect of substituting strongly electronegative groups at tin should be to deshield the gem-proton most, contrary to what is observed. Canonical forms such as $^+CH_2-CH=Sn^-$ involving (p+d)- π interactions and charge separation¹⁶ could rationalize the deshielding of the β -protons and the small effect on the α -proton as well, but this is not a suggestion that we favor. Steric effects would be expected to give rise to temperature-dependent spectra, but no change in the fluorine-19 spectrum of $(C_2H_3)_2Sn(C_2F_5)_2$ was observed to $-120^\circ C$.

Unlike the ethyltin case, the vinyltin-nmr data are much closer to those of tetravinyltin¹⁴⁻¹⁶ than to the vinyltin halides.³⁷

The related ethyltin hydrides are of interest. The proton nmr assignments are listed in Table V. One set of SnCH_2CH_3 satellites and both the tin-117 and tin-119 Sn-H satellites were observable, as was ν_A . A slight discrepancy between the calculated and observed B resonances probably arises as a result of the hydridic proton coupling with the methylene group.

The $|^2J(^{119}\text{Sn-C-}^1\text{H})|$ and $|^3J(^{119}\text{Sn-C-C-}^1\text{H})|$ both increase linearly with the number of ethyl groups at tin as shown in Figure 1. The value of $|^2J(^{119}\text{Sn-C-}^1\text{H})|$ could not be discerned from the spectrum of ethyltin trihydride directly, but its value was estimated from the line in Figure 1, and found in this way. The magnitude of the $|^1J(^{119}\text{Sn-}^1\text{H})|$ values have also been found to correlate with the number of alkyl groups at tin.³⁸

Acknowledgements. Our work is supported by the National Science Foundation and by the Office of Naval Research. We are grateful to M & T Chemicals, Inc. for the donation of organotin starting materials.

Table I

Infrared Absorptions for the Perfluoroethyltin Compounds^{a, b}

$(C_2H_5)_2Sn(C_2F_5)_2$	$(C_2H_5)_2Sn(I)C_2F_5$	$(CH_2=CH)_2Sn(C_2F_5)_2$	$(CH_2=CH)_3SnC_2F_5$	Assign.
2960 s	2965 s	—	2985 m	$\gamma(C-H)$
—	2940 m	—	2943 m	$\gamma(C-H)$
2880 s	2880 s	—	—	$\gamma(C-H)$
—	—	—	1915 w	$\gamma(C=C)$
1520 w	—	—	—	—
1460 m	1462 m	—	—	—
—	1423 w	—	—	—
1385 w	1388 m	1398 vw	1398 m	—
1315 vs	1318 vs	1318 vs	1318 vs	$\gamma(C-F)$

^a $\pm 10\text{ cm}^{-1}$.^b 10% solutions in CH_2Cl_2 .

Table I, cont.

$(C_2H_5)_2Sn(C_2F_5)_2$	$(C_2H_5)_2Sn(I)C_2F_5$	$(CH_2=CH)_2Sn(C_2F_5)_2$	$(CH_2=CH)_3SnC_2F_5$	Assign.
1270 vs	1292 s	1292 w	1290 w	—
1195 vs	1188 vs	1203 vs	1195 vs	$\checkmark(C-F)$
1098 vs	1100 vs	1103 vs	1095 s	$\checkmark(C-F)$
1060 vs	1068 vs	1072 m	1052 s	$\checkmark(C-F)$
1017 m	1023 m	—	1002 s	—
—	958 m	965 w	960 s	—
927 s	930 s	942 s	930 s	$\checkmark(C-C)$

Table II

Mass Spectral Fragments for
Perfluoroethyltin Compounds^a

$(C_2H_5)_2Sn(C_2F_5)_2$			$(C_2H_5)_2Sn(I)C_2F_5$		
M/e ^b	Ion	Abund.	M/e	Ion	Abund.
297	$(C_2H_5)_2SnC_2F_5$	0.33	305	$(C_2H_5)_2SnI$	0.21
287	$C_2H_5Sn(F)C_2F_5$	0.01	295	$C_2H_5Sn(I)F$	0.10
196	$(C_2H_5)_2SnF$	1	247	$(C_2H_5)_2SnCF_3$ or SnI	0.16
186	$C_2H_5SnF_2$	0.27	213	$C_2H_5(C_2H_2F)SnF$	1
149	C_2H_5Sn	0.36	155	CH_2FSnF	1
139	SnF	0.48	149	C_2H_5Sn	0.63
100	C_2F_4	0.007	139	SnF	0.37
			101	C_2F_4H	0.21
			100	C_2F_4	0.21

^aRecorded at an ionization voltage of 20 eV.

^bBased on tin-120.

Table II, cont.

$(\text{CH}_2=\text{CH})_2\text{Sn}(\text{C}_2\text{F}_5)_2$			$(\text{CH}_2=\text{CH})_3\text{SnC}_2\text{F}_5$		
M/e	Ion	Abund.	M/e	Ion	Abund.
293	$(\text{C}_2\text{H}_3)_2\text{SnC}_2\text{F}_5$	0.20	201	$(\text{C}_2\text{H}_3)_3\text{Sn}$	1
285	$(\text{C}_2\text{H}_3)(\text{C}_2\text{F}_5)\text{SnF}$	0.02	193	$(\text{C}_2\text{H}_3)_2\text{SnF}$	0.33
209		0.01	175		0.25
193	$(\text{C}_2\text{H}_3)_2\text{SnF}$	1	147	$(\text{C}_2\text{H}_3)\text{Sn}$	0.45
185	$(\text{C}_2\text{H}_3)\text{SnF}_2$	0.25	139	SnF	0.20
147	$(\text{C}_2\text{H}_3)\text{Sn}$	0.37			
139	SnF	0.42			
108		0.06			
100	C_2F_4	0.05			

Table III

¹⁹F Nmr Assignments for Perfluoroethyltin Compounds ^{a,b}

	(C ₂ H ₅) ₂ Sn(C ₂ F ₅) ₂	(C ₂ H ₅) ₂ Sn(I)C ₂ F ₅	(CH ₂ =CH) ₂ Sn(C ₂ F ₅) ₂
ν_A^c	7888.5	7764.3	7832.5
ν_B^d	10958.5	11094.6	10910.6
J_{AB}^e	not obs.	2.0	not obs.
$ ^2J(^{117}/^{119}\text{Sn-A}) $	<10	<10	3.7 (?)
$ ^3J(^{119}\text{Sn-B})^f $	228.2	241.5	272.8
$J^{119}/^{117g}$	1.045	1.045	1.043

^a 10% solutions in CH₂Cl₂.^b A₃B₂Sn=CF₃CF₂Sn.^c Chemical shifts in Hz relative to CFCl₃.^d ±0.5 Hz.^e ±0.1 Hz.^f ±0.5 Hz.^g Theoretical ratio=1.046.

Table IV

¹H Nmr Assignments for the Perfluoroethyltin Compounds^a

	(C ₂ H ₅) ₂ Sn(C ₂ F ₅) ₂ ^{b,c}	(C ₂ H ₅) ₂ Sn(I)C ₂ F ₅ ^{b,d}	(C ₂ H ₅) ₂ Sn(C ₂ F ₅) ₂ ^{e,f}	(C ₂ H ₅) ₃ SnC ₂ F ₅ ^{e,f}	(C ₂ H ₅) ₄ Sn ^{e,f,g}
^h ν _A	392.6	398.3	633.1	634.6	631.8
^h ν _B	372.5	362.8	640.1	629.0	614.1
^h ν _C	—	—	600.5	585.6	568.6
³ J _{AB} ⁱ	8.0	7.8	13.3	13.2	13.8
³ J _{AC} ⁱ	—	—	20.1	19.9	20.7
² J _{BC} ⁱ	—	—	2.8	3.2	3.1
² J(¹¹⁹ Sn-H _A) ^j	102.6	117.8	129.8	112.0	—
³ J(¹¹⁹ Sn-H _B) ^j	59.4	48.2	246.7	210.8	—
J(¹¹⁹ Sn-H _C) ^j	—	—	116.3	105.5	—

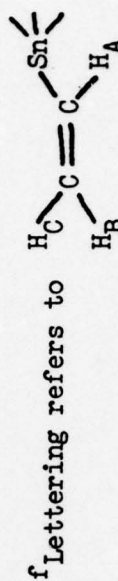
^aIn Hz relative to TMS.^bThe values relative to the CH₂Cl₂ internal standard were converted to TMS using 532Hz; lettering refers to A₃B₂Sn.^cThe tin-119 chemical shift is 65 p.p.m. upfield of tetramethyltin.³⁹^dThe tin-119 chemical shift is 17 p.p.m. upfield of tetramethyltin.³⁹^eRelative to TMS.^gRef. 16.^h±0.2 Hz.ⁱ±0.1 Hz.^j±0.2 Hz.

Table V

¹H Nmr Assignments for the Ethylstannanes

	(C ₂ H ₅) ₄ Sn	(C ₂ H ₅) ₃ SnH	(C ₂ H ₅) ₂ SnH ₂	C ₂ H ₅ SnH ₃
$\nu_A^{a,b}$	120.0 ^c	120.3	125.8 ^d	125.7
ν_B^b	81.5 ^e	85.9	101.1 ^f	—
ν_C^b	—	503.5 ^g	464.8 ^h	431.0 ⁱ
$\nu_{Sn}^{j,k,l}$	-1	40	231	280
$ ^3J(^{119}Sn-A) ^m$	69.2 ⁿ	75.8	82.8 ^o	89.7
$ ^2J(^{119}Sn-B) ^m$	49.7 ^{p,q}	55.2 ^q	60.2 ^q	65.6 ^q
$ ^1J(^{119}Sn-C) ^r$	—	1613.2 ^{q,s}	1689.6 ^{q,t}	1790.4 ^{q,u}
$J_{AB}^{h,n}$	8.2	8.2	8.0	7.8

^aAll chemical shifts are in Hz and are relative to TMS at 100 MHz; CH₃CH₂SnH = A₃B₂SnC.

^b±0.3 Hz.

^c ν_A for (C₂H₅)₄Sn has been listed as -1.08,³⁰ -1.18 (CCl₄/TMS),⁴⁰ -1.21 (CDCl₃/TMS),¹⁸ -1.20 p.p.m. (DMSO/TMS),¹⁸ -70.6 (TMS),⁴¹ -71.0 (CCl₄/TMS),⁴² 6.6 Hz (vs. cyclohexane at 25 MHz),⁴³ and τ = 9.22.⁴⁴

^d ν_A for (C₂H₅)₂SnH₂ has been listed as τ = 8.80.⁴⁵

^e ν_B for (C₂H₅)₄Sn has been listed as -0.69 (CCl₄/TMS),³⁰ -0.74 (CCl₄/TMS),⁴⁰ -0.76,⁴⁶ -0.83 (CDCl₃/TMS),¹⁸ -0.79 p.p.m. (DMSO/TMS),¹⁸ -47.0 (CCl₄/TMS),⁴² 15.9 Hz (vs. cyclohexane at 25 MHz)⁴³ and τ = 8.84.⁴⁴

^f ν_B for (C₂H₅)₂SnH₂ has been listed as τ = 9.17.⁴⁵

^g ν_C for (C₂H₅)₃SnH has been listed as τ = 5.24 (CS₂),⁴⁷ 5.17,³⁸ 5.00 (cyclopentane)⁴⁸ and δ = -293.5 Hz.⁴⁹

^h ν_C for (C₂H₅)₂SnH₂ has been listed as τ = 5.25 (cyclopentane),⁴⁷ 5.38 (10% in TMS),⁴⁵ 5.52 (cyclopentane)^{38,48,50} and δ = -4.59 p.p.m.⁵¹

Table V, cont

ⁱ_vC for $C_2H_5SnH_3$ has been listed as $\tau = 5.66$ (cyclopentane).^{38,47,48}

^jA positive sign indicates a shift upfield of tetramethyltin.

^kRef. 39.

^lThe tin-119 chemical shift for $(C_2H_5)_4Sn$ has been listed as -1.4 (CCl_4),^{52,53} 5.97 ,⁵⁴ 6.0 ⁵⁵ and 6.7 p.p.m.⁵⁶ vs. $(CH_3)_4Sn$.

^m ± 0.2 Hz

ⁿ $|^3J(^{119}Sn-C-C-^1H)|$ for $(C_2H_5)_4Sn$ has been listed as 65.7 ,⁴¹ 66.8 ,⁴³ 69.2 ,⁴² 71.2 ,^{30,44,57,58} 68.5 ($CDCl_3$)¹⁸ and 67.9 Hz (DMSO).¹⁸

^o $|^3J(^{119}Sn-C-C-^1H)|$ for $(C_2H_5)_2SnH_2$ has been listed as -83.7 Hz.⁴⁵

^p $|^2J(^{119}Sn-C-^1H)|$ for $(C_2H_5)_4Sn$ has been listed as 32.2 .^{30,44,57-59}

^qRef. 60.

^r ± 0.2 Hz.

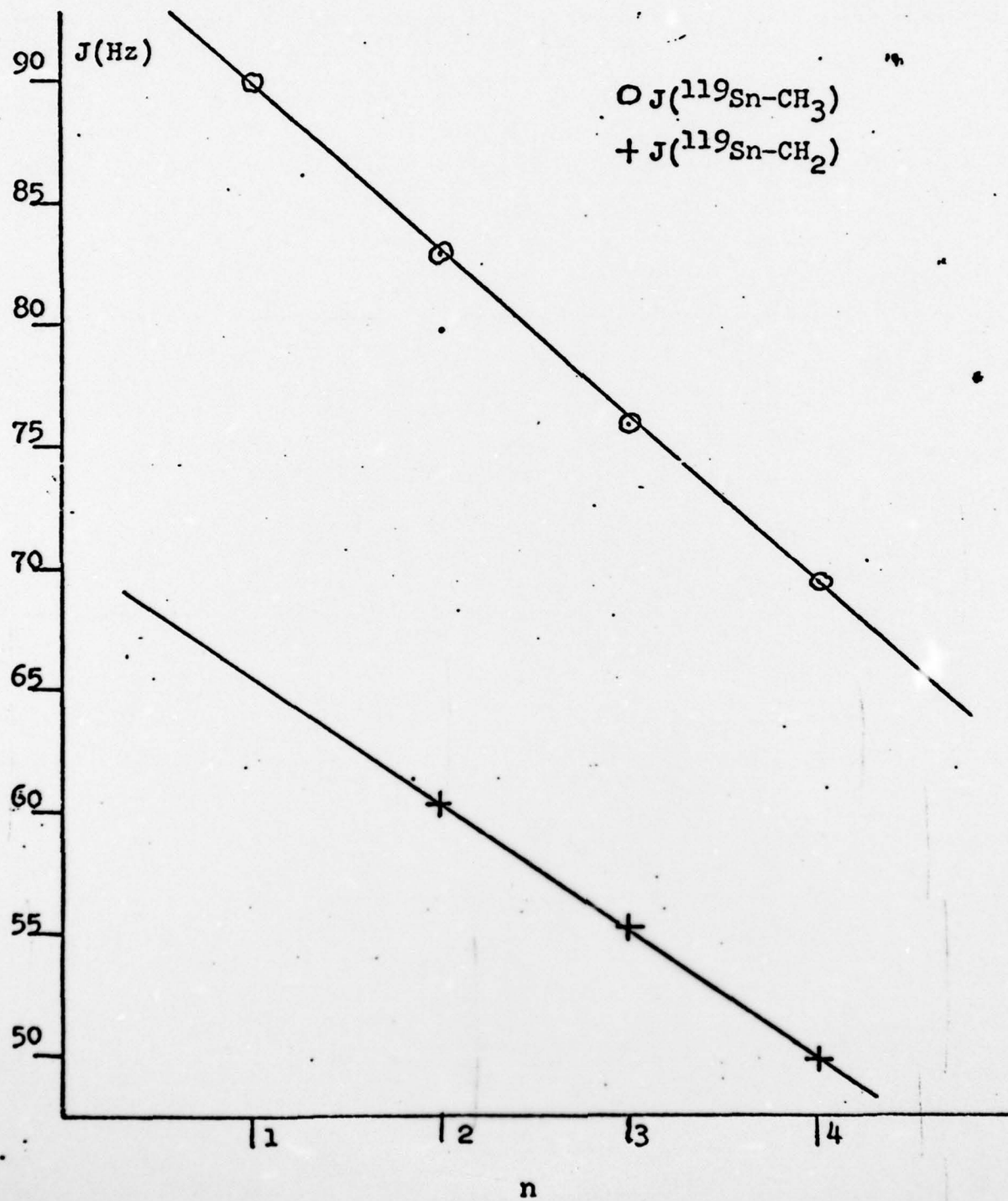
^s $|^1J(^{119}Sn-^1H)|$ for $(C_2H_5)_3SnH$ has been listed as 1574 ,³⁸ 1611.3 ⁴⁸ and 1612.4 ⁴⁹ Hz.

^t $|^1J(^{119}Sn-^1H)|$ for $(C_2H_5)_2SnH_2$ has been listed as -1688.4 ⁴⁵ and 1691.1 ^{38,48,50} Hz.

^u $|^1J(^{119}Sn-^1H)|$ for $(C_2H_5)_3SnH$ has been listed as 1790.1 ^{38,48} Hz.

Figure 1

J values vs. Number of Ethyl Groups, in Ethylstannanes



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